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Polythiophene Derivative with a Side Chain Chromophore as Photovoltaic and Photorefractive Materials

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ABSTRACT:

A new, solution processable, thiophene copolymer with a side chain nonlinear optical (NLO) chromophore namely Poly(3-octylthiophene-co-N-(3-thenyl)-4-amino-2-nitro phenol) [POMDT] has been chemically synthesized. The copolymer was further functionalized with a photocrosslinkable cinnamoyl group, and was doped with a photocrosslinkable NLO dye. The poled, photocrosslinked, dye doped copolymer exhibited relatively large second order NLO effects ($d_{33} = 18.6$ pm/V and 3.3 pm/V at 1.064 μ m and 1.542 μ m respectively). The NLO properties of the photocrosslinked samples were stable at room temperature for 100 hours. The combination of reasonably good second order optical nonlinearity with established photoconducting behavior of the polythiophenes allows these type of polymers to be candidate materials in photovoltaic and photorefractive applications.

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Introduction:

Electrically conducting polymers continue to attract great scientific interest, in some measure due to their expanded melt or solution processability. Application of these types of materials in electronics,¹ power equipments,² sensors,³ and nonlinear optics⁴ for example, has been reported. The polyheterocycles such as polythiophenes and polypyrroles as a class of materials, present special opportunities⁵ because of the possibilities in structural modification and ease of formation by either chemical⁶ or electrochemical⁷ polymerization techniques. The polythiophenes are conjugated conducting polymers with excellent electronic and reasonably good mechanical properties and are stable towards oxygen and moisture at ambient temperatures.^{8,9} Unfortunately, the delocalized electronic structures due to π -conjugation, makes the polymer rigid and intractable. The intractability, in addition with the possible crosslinking at β -position of thiophene during polymerization, makes the polymer insoluble and infusible causing nonprocessability of these type of materials. The processability of polythiophenes can be improved by introducing a flexible side chain of 4 or more carbons at the 3-position of thiophene. The long chain substitution at 3-position of thiophene ring reduces the chain intractability and also the β -coupling during polymerization.¹⁰ The processability is achieved with no sacrifice in conductivity,¹¹ but the conductivity decreases with time especially in the presence of oxygen, and humidity at high temperatures.¹² The stability of these type of materials are enhanced by thermal annealing¹³, by suitably

modifying the structure with the introduction of stable aromatic groups¹⁴ in the side chain and by copolymerization with 3-methylthiophene.¹⁵

Modifications in the chemical and physical properties of conjugated polymers like polythiophenes and polypyrroles are readily achieved by attaching the appropriate functional group in the side chain. The derivitization at the 3-position is easy with the thiophene compared to pyrrole, where the ring nitrogen must be protected in the latter.¹⁶ This makes the thiophene monomer, a suitable material for structural modification,¹⁷ to achieve the desired bulk property in the polymer such as water solubility,¹⁸ optical activity,¹⁹ ionic conductivity²⁰ or liquid crystalline properties.²¹

Recently, photovoltage generation was observed in a poled guest-host system of a second order Non Linear Optical (NLO) chromophore in an inert polymer matrix²² in our laboratory for the first time. The origin of this photovoltage generation is due to a change in polarization of the medium upon photoexcitation, which is similar to photoinduced polarization observed in the Langmuir-Blodgett (L-B) films of donor-acceptor molecules.²³ But due to large internal resistivity of the polymer host, the observed short circuit current is very small in these type of materials. The photo response can be greatly improved by embedding a second order NLO chromophore in a medium where facile charge transport is possible. The chromophores must possess a stable poled order in this matrix.

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The Photorefractive effect in polymers has drawn attention due to the potential applications in image amplification, phase conjugation, 3D optical data storage, etc.²⁴ For photorefractive effect to be present in a material, the presence of photoconductivity, an electrooptic (EO) effect, and small dark conductivity are necessary.²⁵ Photorefraction was recently observed in a number of dye doped non linear organic polymeric systems,^{26,27} by several groups. The NLO chromophore itself was found to be responsible for photoinduced charge generation.^{26a} Small molecular hole transport agents like diethylamino-benzaldehyde diphenylhydrazone,²⁷ 1,1-bis(4-di-p-tolylaminophenyl)cyclohexane were added into the matrix by a number of researchers for the charge transport. The response time of a photorefractive material is strongly dependednt on the photocarrier generation efficiency in a material. Conjugated polymers such as polythiophenes are excellent photo-conductors.²⁸

In this work, we seek to design a stable EO polymer with added functionalities for realizing improved photovoltaic effect and photorefraction. For this purpose the thiophene monomer was functionalized with a NLO chromophore and then was copolymerized with 3-octylthiophene with an objective of producing a processable material which will also show second order NLO response. The copolymer was further functionalized with a photocrosslinkable cinnamoyl group. Upon poling, the second order NLO activity was observed in this NLO copolymer. Furthermore, when this copolymer was doped with a photocrosslinkable NLO chromophore, which

possesses relatively large molecular hyperpolarizability, poled, and photocrosslinked, a stable and greatly enhanced second order optical nonlinearity was measured. The details of the syntheses, structural and thermal characteristics of the copolymer are discussed in this paper. Preliminary results from second order NLO measurements are also presented.

Experimental:

1. Materials:

The 3-octylthiophene was obtained from TCI America. All other reagents were obtained from Aldrich Chemical Co. Inc., and were used without further purification, except the tosyl chloride. The later was recrystallized from petroleum ether before its use.

2a. Synthesis of monomer: N(3-thienyl)-4-amino-2-nitro-phenol (MDT):

The 3-thienylmethanol (3-MT) was tosylated using p-toluene sulfonyl chloride in the presence of dry pyridine²⁹ at -20 °C and was precipitated in ice cold 1N hydrochloric acid. The precipitated tosylate was dried under vacuum and was then recrystallized from petroleum ether, to produce white needle like crystals. The p-toluene sulfonate (tosyl) derivative of the 3-MT (2.68 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) were dissolved in chloroform in a RB flask. A solution of 4-amino-2-nitro phenol (1.62 g, 10.5 mmol) in chloroform was added slowly to the above mixture, with vigorous

stirring. The stirring was continued for 24 hours. The contents of the flask were then poured into 200 mL of ice cold 1N HCl taken in a beaker. The organic layer was separated, washed with 3X25 mL of cold 1N HCl and then with 3X20 mL of distilled water, dried over anhydrous magnesium sulfate and filtered. The solvent from the filtered solution was removed by rotary evaporator under vacuum. The residue gave yellow crystals of MDT upon recrystallization from methanol. Yield 2.2 g (88%). mp 118 °C.. IR (KBr, in cm^{-1}): 3200-3600 (s, $\nu_{\text{O-H}}$), 3100 (w, aromatic $\nu_{\text{C-H}}$), 2960 (w, $\nu_{\text{C-H}}$), 1540 (w, $\nu_{\text{N-O}}$, asymmetric), 1354 (s, $\nu_{\text{N-O}}$, symmetric), 850 ($\nu_{\text{C-N}}$ of NO₂-aromatic carbon). ¹H NMR (CDCl_3 , δ in ppm): 2.4 (s, 2H, $-\underline{\text{CH}_2}-$), 5.3 (s, 1H, $-\underline{\text{NH}}-$), 6.9 (d, 1H, aromatic), 7.1 (m, 2H, aromatic), 7.2 (s, 1H, aromatic), 7.5 (s, 2H, aromatic). UV (λ_{max} , in CHCl_3) : 350 nm

2b. Copolymerization:

The 3-octylthiophene and the monomer MDT (in the molar ratio of 2:1) were copolymerized by chemical dehydrogenation method³⁰ using anhydrous ferric chloride. A 10 mmol solution of comonomer mixture in chloroform was polymerized using 40 mmol of ferric chloride at room temperature under nitrogen atmosphere. After stirring for 48 hours, the copolymer (POMDT21) was precipitated in methanol, filtered, washed with acetone-methanol mixture and then was soxhlet extracted with methanol for 3 days to remove oligomeric and iron impurities. The copolymer was finally washed with aqueous ammonia solution to remove the trace amount of iron impurities. The purified copolymer (yield 90% by weight)

was then dried and was extracted with chloroform to separate the soluble copolymer (95%) from high molecular weight insoluble gel (5%). Anal. C, 66.21; H, 7.19; N, 3.55; S, 15.32; O, 7.14. Calcd for $[(C_{12}H_{18}S)_{0.67}(C_{11}H_8N_2SO_3)_{0.33}]$: C, 67.29, H, 7.27, N, 3.72, S, 15.30, O, 6.38. IR (KBr, in cm^{-1}): 3200-3600 (m, ν_{O-H} & ν_{N-H}), 3100 (w, ν_{C-H} , aromatic), 2922 & 2852 (s, ν_{C-H}), 1542 (w, ν_{N-O}), 1354 (w, ν_{N-O}), 830 (δ_{C-H} out of plane, thiophene ring). 1H NMR ($CDCl_3$, δ in ppm): 0.87 (s, 3 H, $-CH_3$), 1.2-1.5 (broad, 10 H, $-CH_2-$), 1.57 (broad, 2 H, $-CH_2-$), 2.1 & 2.2 (s, 2 H, $-CH_2-NH-$), 2.55-2.85 (s, 2 H, $-CH_2-$, for head to head, head to tail and mixed coupling), 5.3 (s, 1 H, $-NH-$), 6.95-7.1 (m, 1 H, aromatic), 7.2 (s, 1 H, aromatic), 7.5 (s, 2H, aromatic). UV (λ_{max} , $CHCl_3$): 430 nm.

2c. Cinnamoylation of POMDT21:

A solution of 0.55 g (3.3 mmol) of cinnamoyl chloride in 10 mL of chloroform was added slowly with stirring, to a mixture of 2.12 g (3.3 mmol of hydroxyl equivalent) of copolymer and 0.27 g (3.5 mmol) of dry pyridine taken in 30 mL of chloroform, at room temperature. The stirring was continued overnight. The solution was concentrated to 20 mL using rotary evaporator under reduced pressure and was poured into 250 mL of methanol to precipitate the copolymer. The precipitated copolymer was then washed with acetone and dried overnight under vacuum. Yield 2.4 g (60% cinnamoylation). IR (KBr, in cm^{-1}): 1729 (m, $\nu_{C=O}$).

3.Preparation of Samples:

The cinnamoylated copolymer was dissolved in chlorobenzene/toluene (3/1 w/w ratio) mixture, filtered through 0.2 μ Gelman filters and spin coated on indium-tin-oxide (ITO) coated glass slide for second harmonic generation (SHG) measurements. The spin coated specimens were dried overnight under vacuum at 70 °C. The films were then poled to align the chromophores using the corona discharge method.³¹ The aligned chromophores were arrested by [2+2] photocrosslinking of the cinnamoyl groups,³² by exposing the specimen to UV light (254 nm) for 5 min. The polymer becomes insoluble after photocrosslinking. To enhance the second order NLO chromophore concentration and the crosslinking density, the copolymer was dissolved with a photocrosslinkable second order NLO chromophore viz. 3-cinnamoyloxy-4-[4-(N, N-diethylamino)-2-cinnamoyloxy phenylazo] nitrobenzene (CNNB-R) in 3:1 (v/v) chlorobenzene/toluene solvent mixture. The forementioned procedure was repeated to get poled, crosslinked films on ITO coated glass slides. The second order NLO properties of the poled specimens were measured by SHG technique using a Q-switched Nd:YAG laser (at 1.064 μ m) and its Raman shifted line (at 1.542 μ m). The SHG method was also used for investigating the temporal stability of the poled order in the chromophore conjugated conducting polymer system over a period of time.

4.Characterization:

The ¹H NMR spectral data were obtained from Bruker WP-270

NMR spectrometer. The IR spectra were recorded on a Perkin-Elmer 1760X FTIR spectrometer. The Ultraviolet-Visible (UV-Vis) spectra were recorded using a Perkin-Elmer lambda-9 UV/VIS/NIR spectrophotometer. The spectrophotometer was equipped with a variable temperature apparatus to allow the measurements of the spectra at different temperatures.

The number- and weight- average molecular weights were determined using a Gel Permeation Chromatography setup (GPC- Waters Model 510 pump, Model 410 refractive index detector, and model 730 module with 500-10⁵ Å Ultrastyrigel columns in series), relative to polystyrene standards. The column was injected with 100 µL of the copolymer solution in chloroform (1 mg/mL) and was eluted with chloroform.

A Differential Scanning Calorimeter (DSC 2910, TA Instruments) was used at a heating rate of 10 °C/min to record the thermograms of the copolymer. The thermal degradation temperatures (T_d) of the polymers were determined using a Thermogravimetric Analyzer (TGA 2950, TA Instruments, Inc.) at a heating rate of 20 °C/min.

Results and Discussion:

The NLO dye attached monomer N-(3-thenyl)-4-amino-2-nitro phenol(MDT) and the copolymer POMDT21 were synthesized as

shown in Scheme-1. The thiophene derivative MDT can be homo-

Insert Scheme-I

Insert Scheme-II

polymerized, but the resultant polymer is insoluble in common organic solvents and is soluble only in concentrated hydrochloric acid (conc.HCl). The polymer precipitates when the yellowish polymer solution in conc.HCl is diluted with water. The monomer MDT was copolymerized with 3-octylthiophene to improve the processability of the resultant conjugated polymer. Among various compositions tried, the copolymer with the composition 2:1 (3-octylthiophene:MDT) was found to be highly soluble in solvents such as THF, chlorinated solvents, dioxane, toluene, etc., forming reddish brown solution which upon dilution becomes yellow. The copolymer is insoluble in acetone, methanol, and acetonitrile and any of these solvents can be used to precipitate the copolymer. The copolymer was further cinnamoylated as shown in scheme-II. The cinnamoylated copolymer is soluble in common organic solvents in the absence of photodimerization. As expected the cinnamoylated copolymer becomes insoluble upon photocrosslinking at 254 nm.

The GPC results are tabulated in Table-1 and are compared with Poly(3-octylthiophene) prepared under similar conditions. From calculation using the elemental analysis data, a 30 mole% MDT dye functionalized monomer insertion in the copolymer is inferred

Insert Table-1

Insert Fig.1

The IR spectrum was recorded by casting a film on a KBr plate. The presence of the imino and hydroxyl groups were confirmed from the band of stretching frequencies from 3200-3600 cm^{-1} . The presence of nitro group³³ in the copolymer was confirmed from the peaks at 1542, and 1354 cm^{-1} . The peak at 830 cm^{-1} is due to the bending vibration of the backbone proton, which is characteristic of 2,3,5-trisubstituted thiophene ring,³⁴ indicating the existence of a linear polymer chain. A peak at 1729 cm^{-1} appeared upon cinnamoylation of POMDT21, which shows the presence of the dye in the copolymer.

The ^1H NMR (Figure 1) signals at $\delta = 2.85$ and 2.65 ppm correspond to the $\alpha\text{-CH}_2\text{-}$ group of the 3-octylthiophene unit for the head to tail and head to head coupling respectively.³⁵ The intensities of these two peaks suggests the presence of about 15% of head to head coupling of the 3-octylthiophene units in the copolymer. Upto 30% of head to head coupling is reported in the synthesis of poly-3-alkyl thiophene using ferric chloride oxidation method. These results are consistent with the 2:1 ratio of alkylthiophene and MDT in the copolymer. Similarly the peaks at $\delta = 2.1$ and 2.2 ppm correspond to the $\alpha\text{-CH}_2\text{-}$ group of the MDT unit for the head to head and head to tail coupling respectively. The intensities of these two peaks indicate very low amount of head to head coupling amongst MDT units. This is expected due to the steric crowding of the aromatic units. Further

few MDT diads are expected in a random copolymer with the given composition. The peak at $\delta=2.55$, which is not found in the poly(3-octylthiophene) is suggested to be due to the $\alpha\text{-CH}_2\text{-}$ units of the mixed coupling between the 3-octylthiophene unit and a MDT unit. This fairly high intensity peak shows the random nature of the copolymerization. The peak between 6.9-7.1 is not well resolved and has multiplet splitting, which is due to the β -proton of the thiophene ring for various regio-isomeric units in the polymer chain.

Thermal Characterization:

The TGA studies at a heating rate of 20 °C /min (Figure 2) of the copolymer POMDT 21 showed that this polymer is stable up to about 285 °C under nitrogen atmosphere, while the poly(3-octylthiophene) prepared under similar conditions is stable up to 395 °C [the literature value³⁶ agrees with this onset temperature for poly(3-octylthiophene)]. The introduction of dye molecule in poly(3-alkylthiophene) reduces the thermal stability of the polymer by about 110 °C, which is mainly due to the thermal degradation of nitro group at higher temperatures. A number of other nitro group containing dye functionalized polymers are also reported³⁷ to start degrading at around 280 °C. The copolymer also yielded a higher char at temperatures above 600 °C compared to poly(3-octylthiophene), which is due to the high C/H ratio of the aromatic unit of the dye.

The DSC thermogram of the copolymer at a heating rate of 10 °C/min, has been shown in Figure 3. While the Poly(3-octylthiophene) shows a weak single melting endotherm³⁸ in the temperature range of 130-150 °C, the new copolymer shows two

Insert Figure 2

Insert Figure 3

melting endotherms at 140 °C and 192 °C respectively, in addition with a weak glass transition at -10 °C. This result shows the possible presence of two different crystalline phases in the copolymer.

Solvato- and Thermo-chromic studies:

The UV-Vis spectra of the copolymer in chloroform and in solid state are presented in Figure 4. The copolymer showed an absorption maximum at $\lambda_{\text{max}}=430$ nm in chloroform with a tail extending up to 550 nm indicating the presence of extended conjugation and multiple conjugation lengths along the main chain of the polymer. The polymer showed a λ_{max} of 520 nm with two shoulders at 604 nm and 552 nm similar to poly(3-alkylthiophenes) in the solid state. The copolymer shows solvatochromic (chloroform

Insert Figure 4

Insert Figure 5

Insert Figure 6

is a good solvent for the POMDT21, there is a red shift of about 90 nm upon addition of a non solvent such as methanol, acetone and

acetonitrile, etc., to the dilute polymer solution) and thermochromic effects as shown in Figures 5 & 6 respectively. The results are similar to that obtained for poly(3-alkylthiophenes),³⁹ which can be explained on the basis of high molar concentration of the 3-octylthiophene units present in the copolymer.

Second Harmonic Generation measurements:

The second order NLO coefficient " d_{33} " of the poled and photocrosslinked polymer film was measured using the SHG technique. The photocrosslinking was done to stabilize the poled order. The general schematic of the photocrosslinking process is shown in Scheme-III. The experimental arrangement for the SHG measurement is reported elsewhere.⁴⁰ The d_{33} coefficient of the polymer sample was measured with a Y cut quartz crystal⁴¹ as a reference ($d_{11}=0.5$ pm/V).

Insert Scheme-III

Insert Figure 7

The poled and photocrosslinked cinnamoylated POMDT film showed a small SH signal, due to very low concentration and molecular hyperpolarizability of the NLO dye used in the copolymer. The copolymer was also doped with 17 % by weight of CNNB-R, whose structure is shown in Figure 7. The poled, and photocrosslinked, CNNB-R doped cinnamoylated POMDT exhibited a large SH signal (the " d_{33} " values of the poled, and photocrosslinked, CNNB-R doped conducting polymer film were determined to be 18.6

pm/V at 1.064 μm and 3.3 pm/V at 1.542 μm). The temporal behavior of the second order NLO properties of the poled polymer films with and without photocrosslinking was investigated by

Insert Figure 8

monitoring the decay of SH intensity at 532 nm as a function of time after poling. Figure 8 shows the relaxation behavior of SH intensity of the dye doped polymer films at room temperature. It is clear that the poled, and photocrosslinked polymer sample exhibits significantly enhanced stability of the SH intensity compared to the uncrosslinked sample. This is expected due to the frozen in alignment of the chromophore by the photocrosslinking process as reported earlier.³²

Conclusions:

We have synthesized a novel, solution processable, photocrosslinkable, polythiophene derivative -POMDT, with a second order NLO chromophore as a side chain. ^1H NMR studies, FTIR spectral data and the thermogravimetric analysis clearly demonstrated the incorporation of NLO species in the conducting copolymer. The DSC thermogram showed two melting endotherms which were attributed to the coexistence of two differently ordered structure in the bulk amorphous state. The copolymer showed low second order NLO activity. Large second order optical nonlinearity was obtained by doping the cinnamoylated POMDT with a photocrosslinkable NLO chromophore. The poled, photocrosslinked,

and dye doped copolymer exhibited good temporal stability at room temperature. We are presently investigating the photoconductive, photovoltaic and photorefractive properties of the POMDT and dye doped POMDT systems. Results from these studies will be reported in a subsequent communication.

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Captions for figures

Figure 1. ^1H NMR spectrum of POMDT21.

Figure 2. TGA diagrams of POMDT21 and Poly(3-octylthiophene) at a heating rate of 20 °C/min.

Figure 3. DSC thermogram of POMDT21 at a heating rate of 10 °C/min.

Figure 4. UV-Vis Spectra of POMDT21 1. in Chloroform (0.0233 mg/mL) 2. of spin coated film.

Figure 5. Optical absorption Spectra of POMDT21 by mixing a solution of polymer in chloroform with methanol at different ratios of chloroform/methanol (v/v). (1) 10/0, (2) 9/1, (3) 8/2, (4) 7/3, (5) 5/5, (6) 1/9. All the measurements were done at 22 °C.

Figure 6. Optical absorption spectra as a function of temperature of a thin film of POMDT21 cast on ITO glass slide.

Figure 7 Chemical structure of photocrosslinkable CNNB-R dye

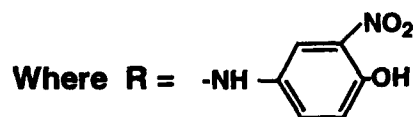
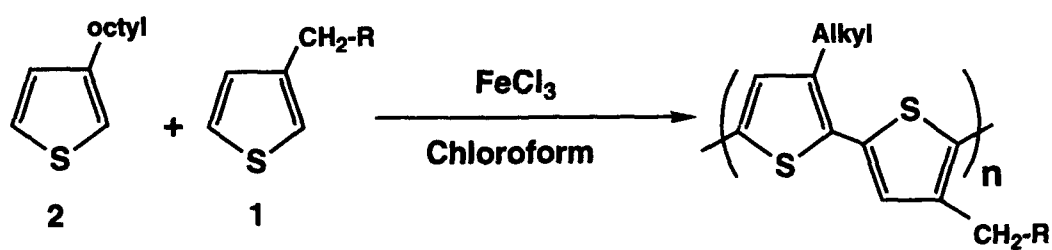
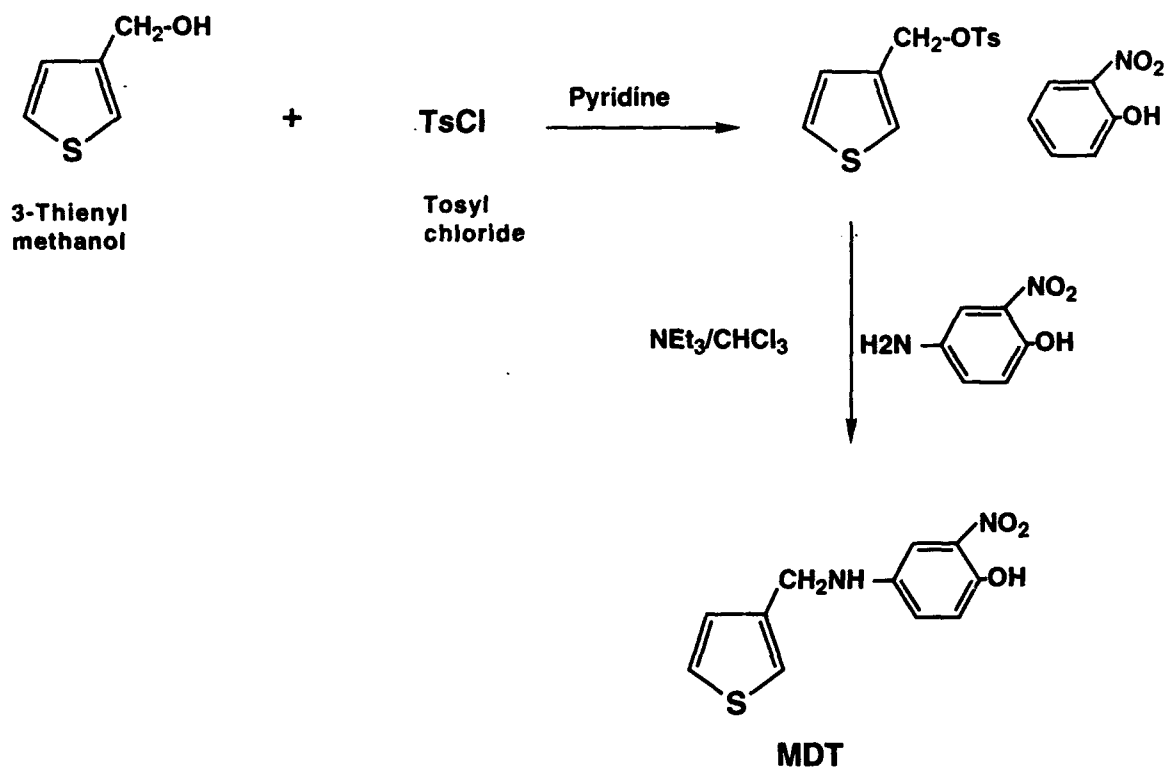
Figure 8. Temporal behavior of the second harmonic intensity of the CNNB-R doped POMDT21 at room temperature.

Table 1: Gel Permeation Chromatographic results of POMDT21 and Poly(3-octylthiophene).

	POMDT21	Poly(3-octylthiophene)
1. Monomer:Ferric chloride ratio	1:4	1:4
2. Reaction time (in hours)	12	12
3. M_n (in g/mole)	20,000	40,000
4. M_w (in g/mole)	81,000	87,000
5. PDI*	4.05	2.18

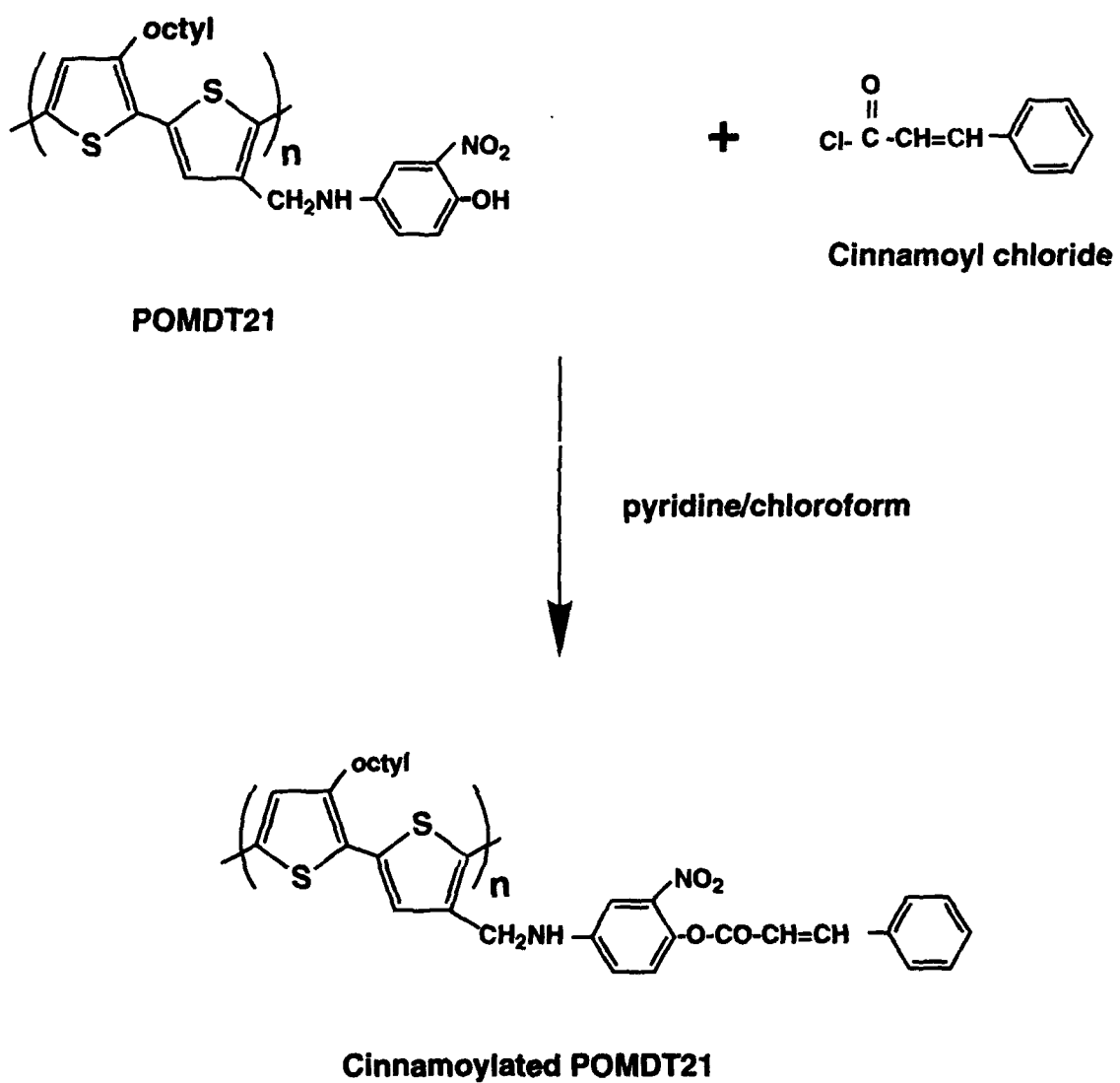
* The polydispersity index (PDI) for the poly(3-octylthiophene) is low compared to the literature values. This might be due to the Soxhalet extraction with acetone, used in the sample purification step, which dissolves most of the oligomers.

Scheme I : Syntheses of monomer MDT and copolymer POMDT21

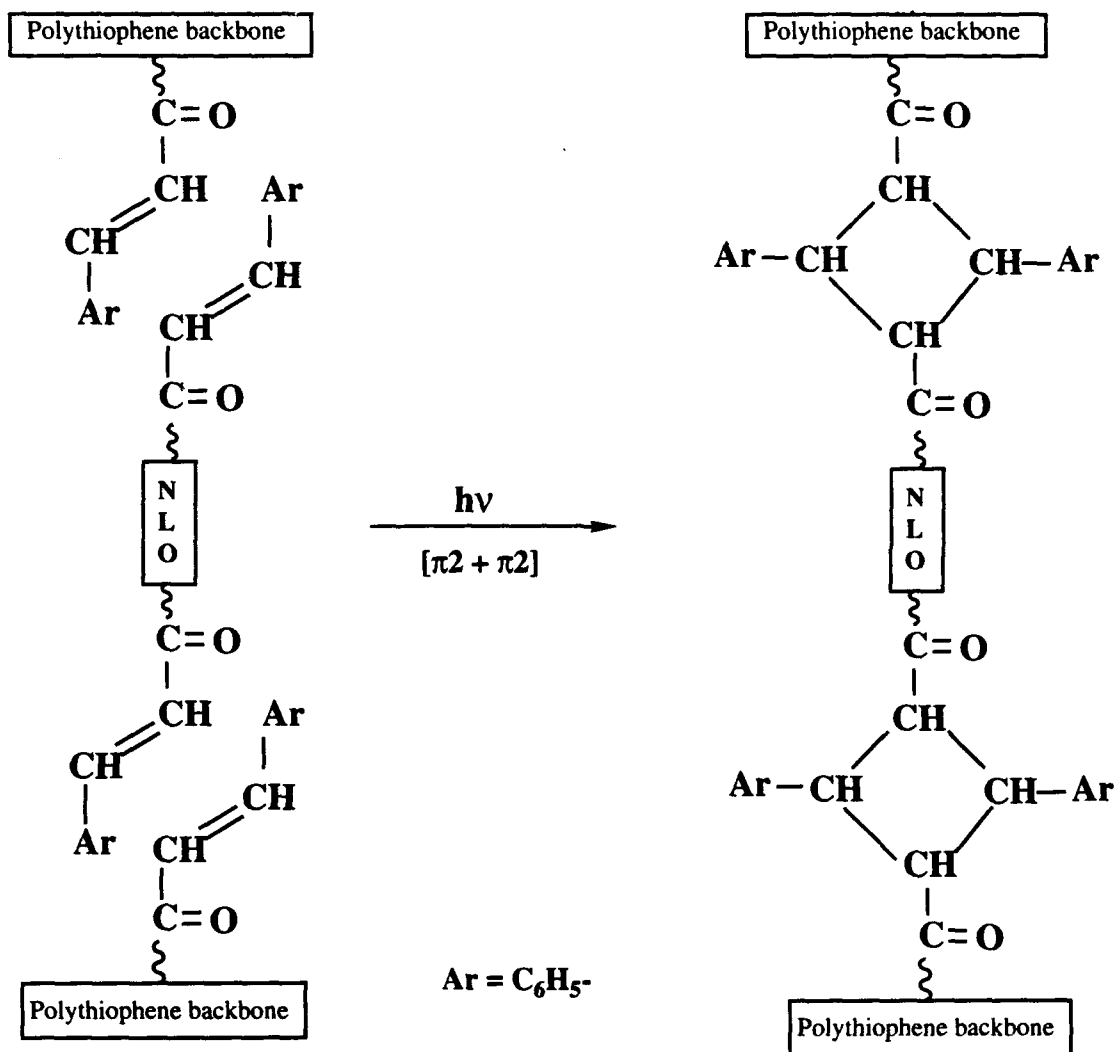


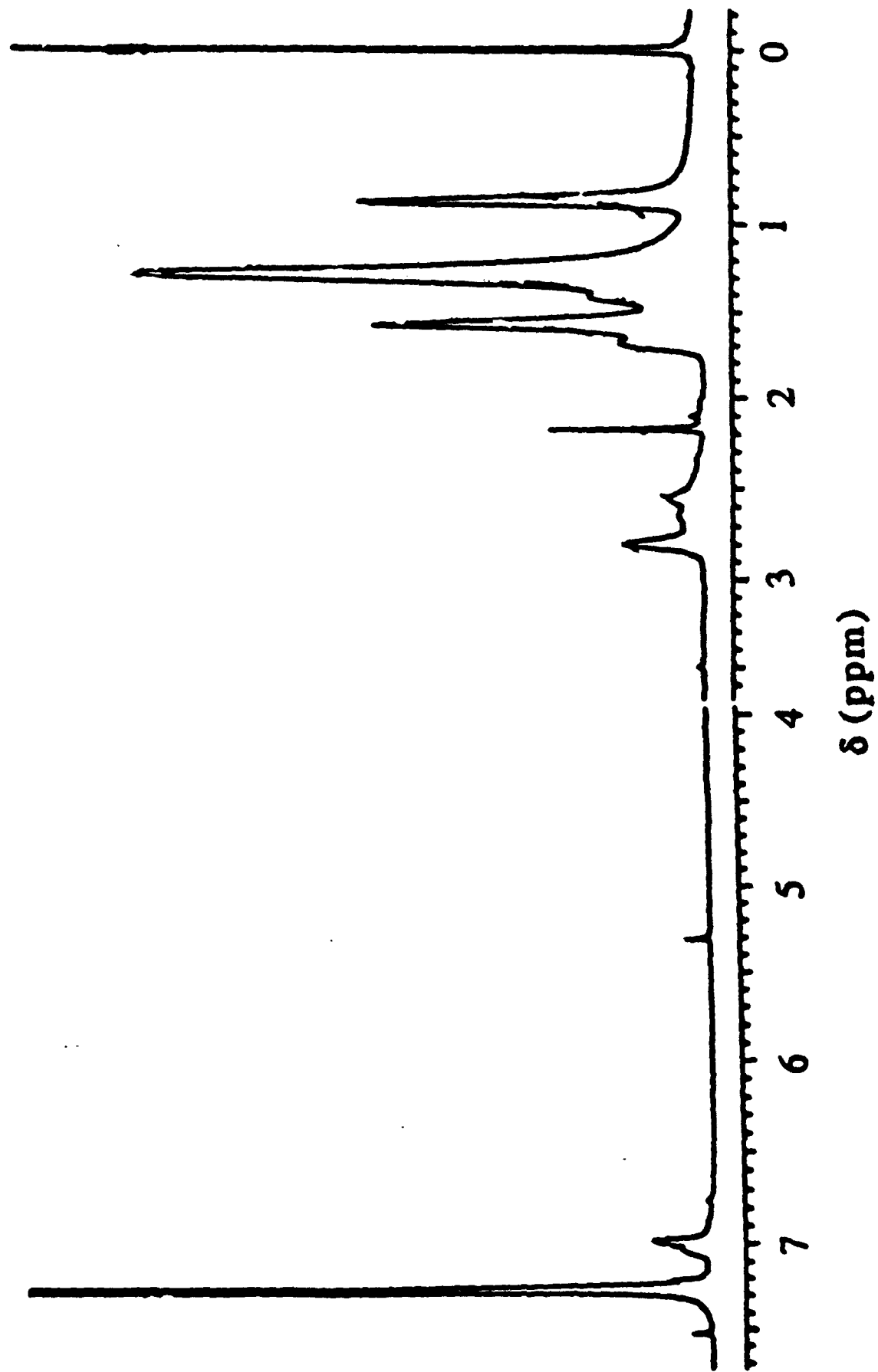
POMDT21

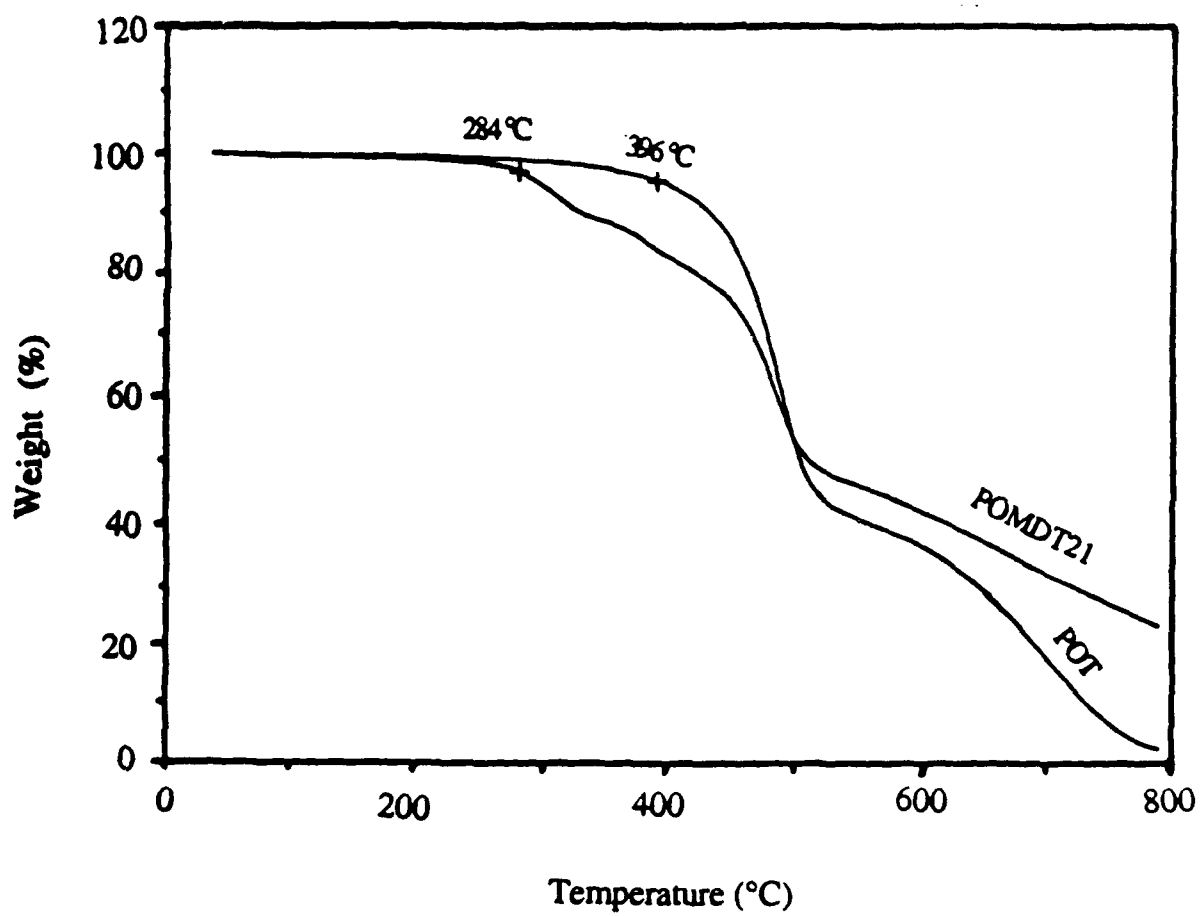
Scheme II : Cinnamoylation of POMDT21

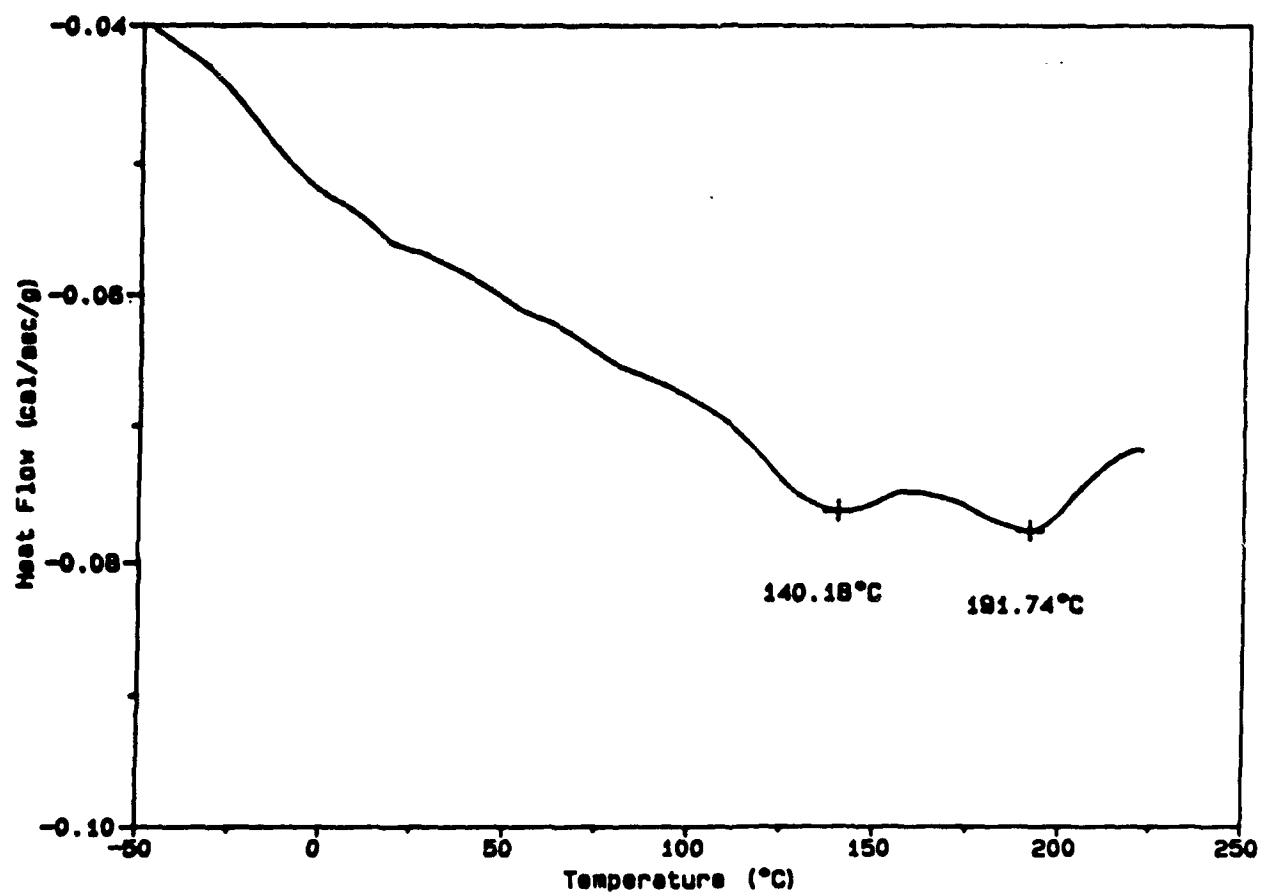


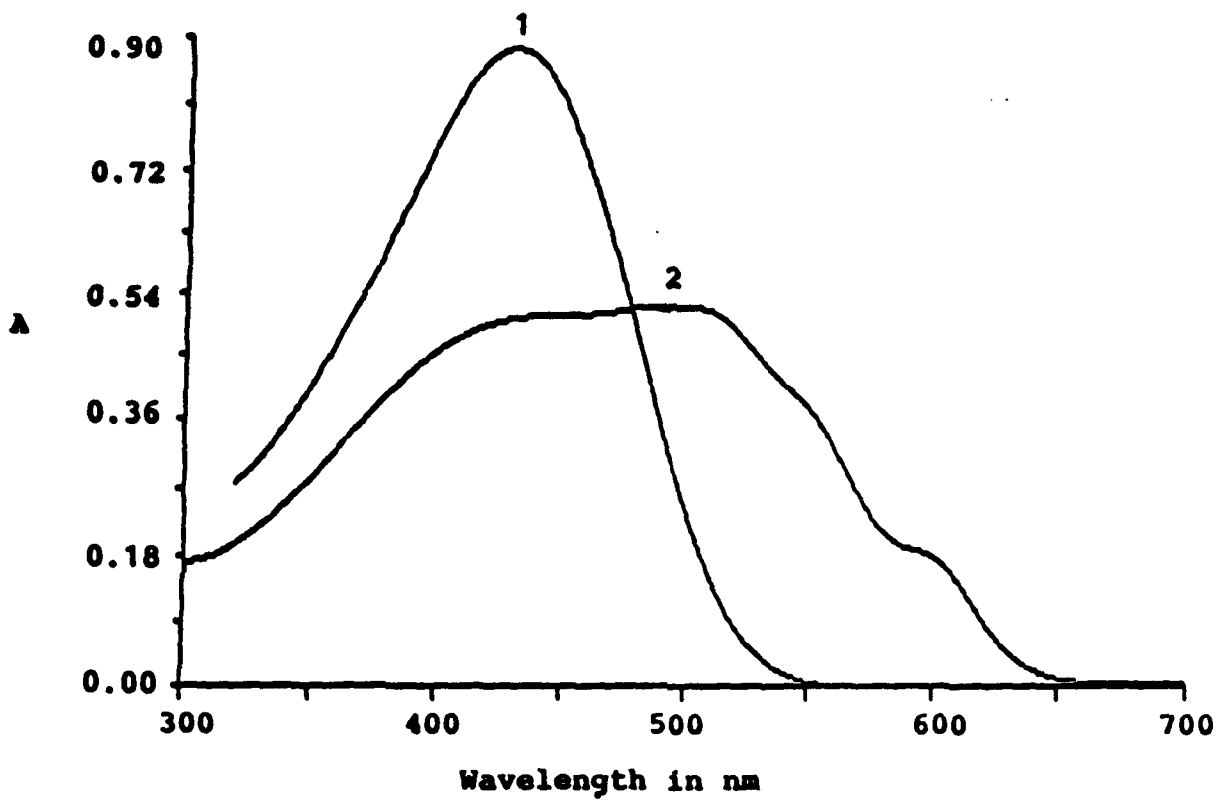
Scheme III : Photocrosslinking reaction between cinnamoyl moieties present in POMDT 21 and CNNB-R dye

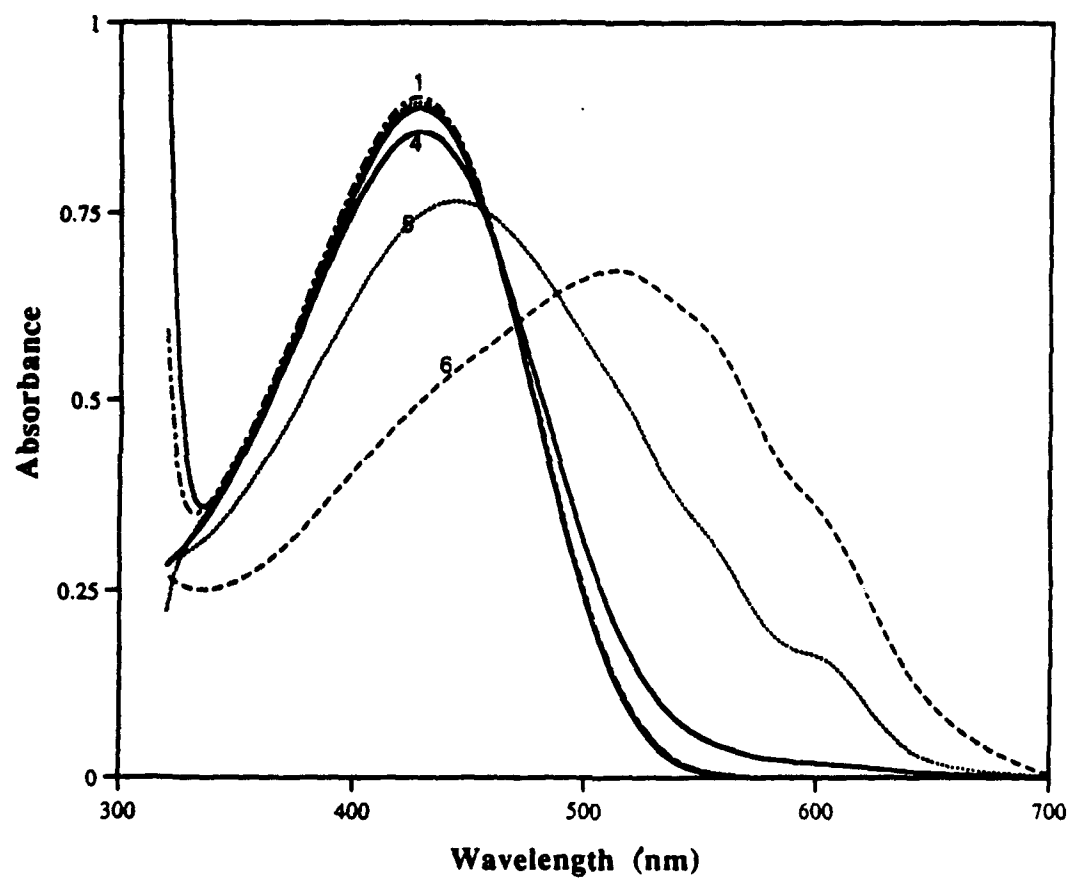


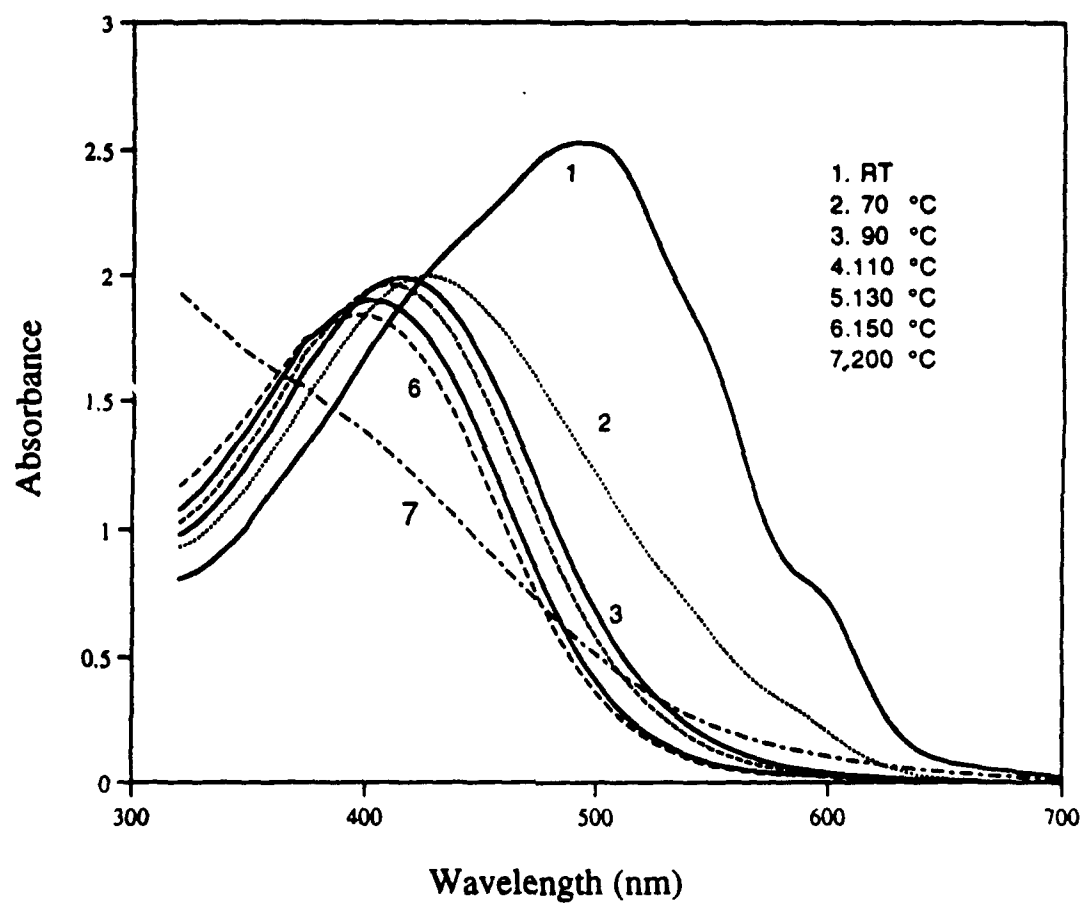


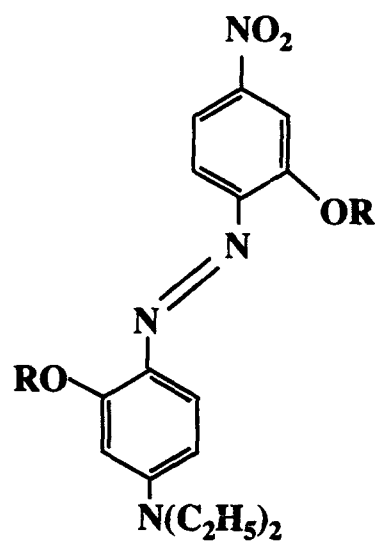


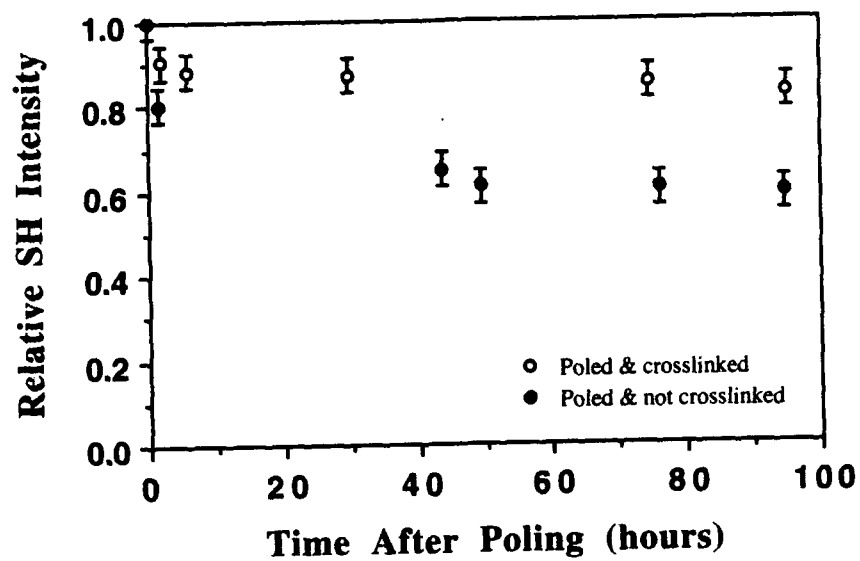












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